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Atomic force microscopy of layer-doped triglycine sulfate ferroelectric crystals

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Despite the long history of the study, ferroelectric crystals of triglycine sulfate $(N^+H_3CH_2COOH)_2(N^+H_3CH_2COO^-)SO_4^{2-}$ (TGS) continue to attract the attention of researchers both as model objects and as potential materials for IR detectors, piezoelectric sensors, pyrovidicones, etc. The introduction of impurities makes it possible to modify effectively the properties of TGS. Thus, chromium (interstitial impurity), although slightly distorts the lattice, but affects significantly the physical properties of crystal. An additional tool for influencing the properties of TGS is the regularly inhomogeneous introduction of Cr^{3+} impurity into the growing crystal by periodically changing the composition of crystallization solution. In this way, the periodic growth structure of alternating stripes of TGS and TGS+Cr with different density of domain walls (impurity layers are characterized by a specific finely dispersed domain structure) and presumably possessing different conductivity is formed. Striped crystals TGS – TGS+Cr are distinguished by high unipolarity and stability of ferroelectric characteristics.

In this work domain structure and impurity distribution in TGS – TGS+Cr crystals was studied with different electrical AFM methods: microscopy of piezoelectric response (PFM), scanning capacitance force microscopy (SCFM), Kelvin probe force microscopy (KPFM), conducting AFM (c-AFM). Also, the nanorelief and mechanical properties of crystals with AFM. The search of new opportunities for local diagnostics of the domain and defect structure of ferroelectrics determined our interest to the work. Also the crystals were studied with X-ray fluorescence (XRF) analysis method, since it provides complete and reliable information about the elemental composition of heterogeneous samples.

The object of study was triglycine sulfate single crystals with a profile distribution of chromium ion impurities (Cr^{3+}) obtained at the Institute of Technical Acoustics. The crystals were grown by a velocity method at a constant growth temperature of 31.4 °C (Curie temperature of TGS = 49.15 °C), the supersaturation of the pure solution was 0.1 °C, the solution with an admixture was 0.5 °C. A periodic change in composition was achieved by incrementing the seed alternately in solutions of different composition – in a nominally pure and containing dopant of chromium ions. The concentration of chromium in the solution was in the range 5-6 wt.%. The growth time of the seed in one cycle was 1.5 hours in a clean solution, and 4.5 hours in an impurity solution.

For AFM investigations samples (1.5-2 mm thick) were obtained by fresh cleavage along the (010) plane, for which the bars with the major axis parallel to the ferroelectric axis b were cut from the growth pyramid of the face m. All experiments on the preparation and precision study of the surface of samples were carried out under strictly controlled conditions of the TRACKPORE ROOM-05 measuring complex, a class of purity of 5 ISO (100) with a humidity of 35 ± 1 rel.% and temperature of 24 ± 0.05 °C, which is especially important in the study of the electrical characteristics of ferroelectrics, the results of which can be significantly affected by water adsorbed on the surface of the sample. The crystals were investigated with NTEGRA Prima scanning probe microscope (NT-MDT SI) using Si tip with Pt coating HA_FM/Pt (Tipsnano, Estonia). Tip curvature radius was R = 35 nm; the cantilever stiffness k ~ 3.5 N/m, and resonance frequency f ~ 77 kHz.

For X-Ray Fluorescence Analysis the TGS − TGS+Cr crystal sample was installed in a DRSh diffractometer. The sample was mounted on an adjusting table so as to make the growth strips lie in the horizontal plane along the incident X-ray beam. The size of the sample surface area exposed to the beam was ~150 μm in the vertical direction and ~5 mm in the horizontal direction.

Then the fluorescent detector was tuned to measure the intensity of the Kα chromium line, and the dependence of the intensity on the vertical sample position, i.e., the position of the area exposed to the X-ray beam at the side crystal face, was recorded. The sample displacement step was ~0.1 mm, and the measurement range was from 0 to 6.5 mm. Simultaneously, the intensity I of the radiation transmitted through the crystal and falling onto a scintillation detector was determined as a function of the exposed spot position on the sample.

While PFM (Fig. 1a) and KPFM (Fig. 1c) allows to observe only domain structure in SCM contrast (Fig. 1b) are formed both on domain walls and on impurity bands It was shown that the capacitance image contrast is formed in the impurity gradient regions, on domain walls. The SCM technique, which is based on measuring the capacitance spatial variation and is highly sensitive to the presence of impurities, allowed us to observe growth impurity strips in the ferroelectric crystal independent of the domain structure and establish a correlation between the defect and domain structures. The SCM technique was shown to be a promising tool for studying the heterogeneous ferroelectric surface, which makes it possible to detect simultaneously images from impurity gradient regions and domain walls and gain insight into the correlation between the domain and defect structures.

XRF analysis was used for the first time to analyze quantitatively the composition of ferroelectric TGS crystals with growth impurity strips. This technique allowed us to determine with a high accuracy the Cr concentration in strips and reveal a periodic impurity distribution. The difference between the chromium concentrations in pure and impurity strips was found to be ~0.08 wt.%, which yielded a difference of 0.17% between the capacitance image contrasts.

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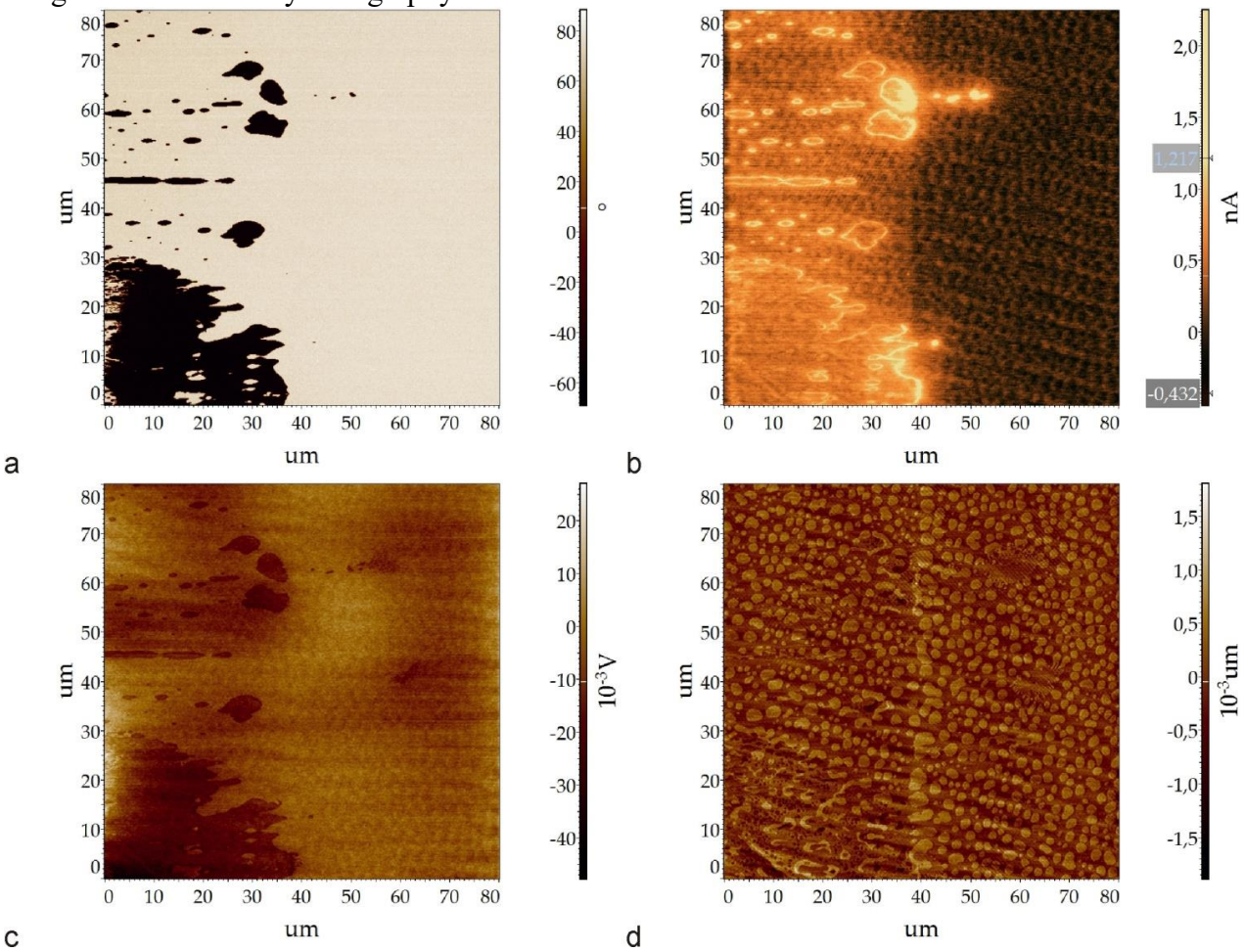

Figure 1. The image of the same surface area of TGS-TGS + Cr crystal with the TGS + Cr stripe (left) and TGS (right): (a) PFM, (b) SCM, (c) KPFM, (d) AFM contact mode, topographic image. The size is 100 × 100 μm.